Starch/Stärke 54 (2002) 20–24

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Film Formation Properties of Potato Starch Hydrolysates

Native and freeze-dried potato starch granules were partially hydrolysed to produce maltodextrins with dextrose equivalents (DE) 10, 15 and 20. Freeze-drying greatly improved the enzyme accessibility of the native granules. Film formation properties of the hydrolysates were examined. Films were prepared by water casting. Especially the maltodextrins, which were produced from the native starch, were very sticky materials and could not form any films. But after removing most of the soluble saccharides from the maltodextrins, good quality films were produced by dissolving the hydrolysate in water, casting on a Teflon mould and drying the solution.

Keywords: Starch; Maltodextrin; Film formation; Glass transition

Research Paper

1 Introduction

Film formation behaviour of cereal and tuber starches has been the focus of many studies during the last decade [1–3]. Suggestions that starches could function as protective edible films and coatings due to their oxygen and aroma barrier characteristics have also been presented [4]. In order to exploit their beneficial properties, starches should be processed economically, i.e. by using feasible technologies under proper processing conditions. When producing coatings from starches, starch polymers must first be dissolved in a solvent, preferably water, and then the solution can be applied on a specific surface, for example by spraying. Despite their hydrophilic character native starches do not dissolve in water easily because of their large molecular size and strong hydrogen bonding. The dissolution in water can be performed only at low starch concentrations and at temperatures above 100 °C [5]. These conditions are not very economical. Starch can be dissolved in water at higher concentrations after partial depolymerisation, which can be achieved with acid or enzymatic treatments.

Amylases are often used for depolymerisation of starches in the preparation of maltodextrins, which are starch hydrolysates with a dextrose equivalent (DE) below 20 [6]. When performing partial hydrolysis of starch with the aid of α-amylase, glucose polymers are randomly attacked, and a variety of oligosaccharides are formed. In the production of maltodextrins most reaction products should be molecules larger than maltose and maltotriose [7]. Although maltodextrins have been industrially produced for decades, relatively few studies have been reported about their structure and physicochemical behaviour. Studies on film formation properties of starch hydrolysis products have not been reported, but film formation is often claimed to be a beneficial property when using maltodextrins as shell materials in encapsulation applications [8, 9]. Sugars in low concentration have been shown to plasticise starch [10], and this indicates that low-molar mass reaction products, which are produced during hydrolysis, may greatly affect the properties of maltodextrin films.

This study was focused on film formation properties of potato starch hydrolysates because of the bland taste and non-cereal character of potato starch. Hydrolysates were prepared by α-amylase treatment of starch granules. The aim was to investigate the processing conditions of these hydrolysates in film casting and the properties of the fresh films.

2 Materials and Methods

2.1 Materials

Potato starch was kindly donated by Järviseudun Peruna (Vimpeli, Finland). Freeze-dried potato starch was prepared by suspending the commercial potato starch (10% w/v) in water at room temperature. The solid fraction was separated by centrifugation and freeze-dried.

2.2 Methods

2.2.1 Preparation of starch hydrolysates

Thermostable α-amylase (Megazyme International Limited, Bray, Ireland) solution was added to native and freeze-dried potato starch-water suspensions (10% starch concentration) using enzyme dosages of 2500–3500 and 225–325 U per gram of starch, respectively. The enzyme dosages were chosen such that starch hydrolysates with DE 10, 15 and 20 could be prepared from both native and freeze-dried potato starches. For DE determination, 20 mL distilled water, 10 mL aqueous solution of copper sulphate (6.9%, w/v) and 10 mL aqueous potassium sodium tartrate solution (3.46%, w/v) were

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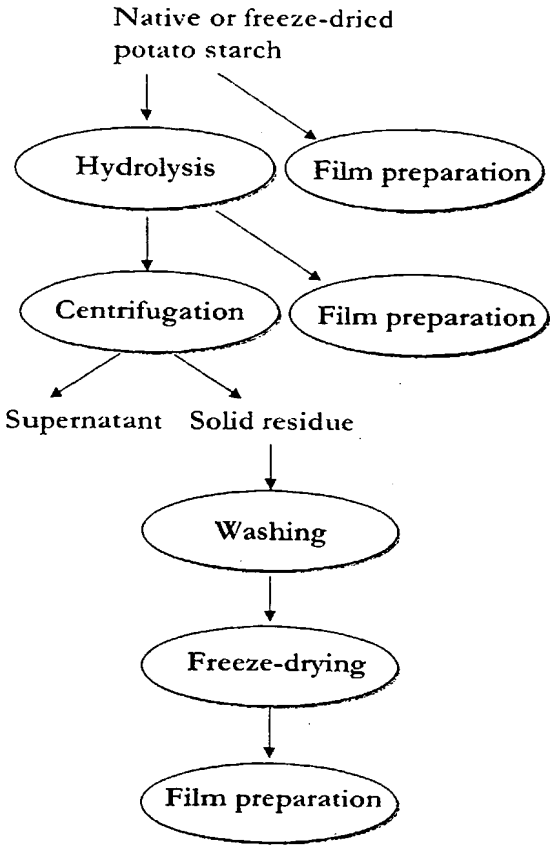

Fig. 1. Scheme for the preparation of the samples for the film processing.

added to 5 mL of the hydrolysate and then boiled for 2 min. Subsequently 10 mL 30% aqueous potassium iodide, 10 mL 25 % sulphuric acid solutions and 2 mL soluble starch were added to the mixture and titrated with 0.1 M sodium thiosulphate under magnetic stirring. The DE value was calculated based on consumption of thiosulphate and dry weight of the original starch sample.

Residual insoluble starch yield was evaluated by separating the insoluble material from the hydrolysate by centrifugation at 10 844 × *g* for 15 min (Fig. 1). The solid residue was washed twice with distilled water, freeze-dried and weighed. The yield was calculated by dividing the mass of the solid residue by the mass of the original starch. This was also the procedure applied for preparation of the solid residues for film casting.

2.2.2 Film preparation

Films were prepared from starch-water dispersions by casting. Starch concentration and temperature in the casting process depended on the starch sample used. The unhydrolysed starches were dissolved in water at 160 °C using a starch concentration of 2%. The concentrations used for the hydrolysates and solid residues were 10% and 20%, respectively, and both dispersions were dissolved at 120 °C. After dissolution the aqueous solutions were poured into prewarmed Teflon moulds and dried at 60 °C. The drying time was 5 h for the native and freeze-dried starches as well as for the hydrolysates, and 24 h for the solid residues. The fresh films were stored for one week at 50% RH and 20 °C prior to testing.

2.2.3 Analysis of molar mass of starch, amylose, sugar and water contents

The solid residues of the hydrolysed potato starches were analysed by size-exclusion chromatography (SEC) as described by *Suortti* and *Pessa* [11]. Native potato starch and the solid residues (50 mg) were suspended in 1.25 mL distilled water and dissolved by addition of 1.25 mL 2 N NaOH with magnetic stirring for at least 6 h at room temperature. Sample preparation was carried out under argon blanket. Resolution of SEC was improved by addition of a third column (μHydrogel 500, Waters Milford, MA, USA) in series with the initial column bank which consisted of μHydrogel 200 and 5000 columns. A dual angle laser light scattering detector (PDI 2000, Precision Detectors, Amherts, MA, USA) was used for determination of the absolute molar mass. Pullulan standards (Shown Denko, Tokyo, Japan) were used to calibrate the laser light scattering detector.

Amylose content was determined colorimetrically according to the method of *Morrison* and *Laignelet* [12]. Sugar content (glucose, maltose and maltotriose) was quantified by HPLC on a Dionex CarboPac column with pulsed amperometric detection (Dionex DX 500, Sunnyvale, USA) equipped with an electrochemical detector (Dionex ED 40). D(+)-glucose (Fluka 49139, Fluka, Buchs, Switzerland), D-maltose (Serva 28390, Serva, Heidelberg, Germany) and maltotriose (Fluka 63430) were used to calibrate the Dionex system. As an internal standard fucose (Fluka 47880) was applied. The water content of the starch films was determined by Karl-Fischer titration (Mettler DC 18, Greifensee, Switzerland). One hundred milligram samples of powders, which were produced by grinding the films with a Fritsch Pulverisette Mill (Idar-Oberstein, Germany), were mixed with 1 mL methanol and stirred in septum-sealed vials for 4 h. After the extraction, a dried syringe with a needle was used to inject 500 μL of the methanol phase into the Karl-Fischer vessel for titration.

2.2.4 Determination of glass transition temperature

A differential scanning calorimeter (Mettler DSC 30, Switzerland) was used to measure the glass transition

temperatures (T_g) of the films. Small pieces of the conditioned films (8–15 mg) were weighed into standard pans (Mettler ME–27331) and the measurements were carried out at a rate of 10 °C/min using an empty pan as reference. The glass transition temperature was taken from the second heating thermogram as the midpoint of the transition.

3 Results and Discussion

Freeze-drying improved greatly the accessibility of potato starch granules to α-amylolysis. The enzyme dosage needed to produce hydrolysates with DE values of 10, 15 and 20 from freeze-dried granules was 10% of that needed for the native granules. Thus potato starch granules were observed to be very resistant to α-amylase, which is well known and has been reported earlier [13, 14].

Gelatinisation is a method to increase the susceptibility of cereal and tuber starches to amylolysis [15–18]. In addition to this heat-moisture treatment, the effect of freezing on the properties of potato starch granules was recently investigated [19]. Potato starch granules with low water contents were frozen under liquid nitrogen, and this treatment affected both the surface structure and re-hydration characteristics of the granules. In the present study changes on the granule surface and of the granular structure may have affected the enzyme accessibility of the granules.

Films were prepared from potato starches and from their hydrolysates (Fig. 1). The films produced from unhydrolysed potato starch were semitransparent and brittle. To achieve good dissolution of the starch polymers only a low starch concentration in the dispersion was used (2%), and the treatment was performed at a high temperature (about 160 °C). The film prepared from freeze-dried starch was somewhat more transparent and not as brittle as the one from native starch, indicating better solubility of the starch polymers due to changes of the granular structure during freeze drying.

Film preparation was difficult when starch hydrolysates including all small hydrolysis products were used (Fig. 1), especially in the case of the hydrolysates made of native potato starch. The preparation difficulties must have resulted from a high content of water soluble glucose molecules in the hydrolysates (see yields in Tab. 2), and probably in the native starch hydrolysate the quantity of small saccharide molecules was larger. The cases in which film formation was successful and the glass transition temperatures and water contents of the cast films are listed in Tab. 1. Even if the films were sticky, one benefit was achieved as the result of the hydrolysis; 10% solids could be used in the water dispersion of film casting.

Tab. 1. Film formation, glass transition temperature (T_g) and water content of native (N) and freeze-dried (FD) potato starch hydrolysates with DE 10, 15 and 20.

Sample	Film formation		T_g [°C]		Water content [%]	
	N	FD	N	FD	N	FD
Hydrolysate (10)	+	+	31	64	13	13
Hydrolysate (15)	–	+	–	49	–	12
Hydrolysate (20)	–	+	–	19	–	13

+ means that film preparation was successful.

Since the hydrolysates produced only very sticky films or film formation was not possible at all, most of the sugars and small oligosaccharides were removed from the hydrolysates by centrifugation and washing (Fig. 1). Based on gravimetric analysis, 22–42% of starch was removed in the centrifugation step (Tab. 2), indicating that this material consisted of water soluble oligosaccharides produced by hydrolysis. Film preparation from the solid residues was rather easy. Solutions with as high as 20% solids content could be used in film casting, and the dissolution procedure could be carried out at only 120 °C. The films prepared in this way from the native and freeze-dried samples differed especially in their stickiness. The films from the freeze-dried starch hydrolysates had a better quality, being non-sticky, transparent and having good mechanical strength.

Average molar mass, amylose, sugar (glucose, maltose and maltotriose) and water contents as well as glass transition temperatures of the solid residues or solid residue films were analysed in order to link the visual observa-

Tab. 2. Yield, amylose and sugar content of the solid residue separated from native (N) and freeze-dried (FD) potato starch hydrolysates with DE 10, 15 and 20. Unhydrolysed starch is shown for comparison.

Sample	Yield [%]		Amylose content [%]		Sugar content [%]	
	N	FD	N	FD	N	FD
Potato starch	100	100	28	28	–	–
Solid residue (10)	78	75	23	24	3.3	1.3
Solid residue (15)	67	64	22	20	4.7	2.6
Solid residue (20)	61	58	19	16	6.4	5.5

tions with the measured data. Based on the SEC analysis, the high molar mass amylopectin, which eluted between 25 to 60 min, and which was observed in the chromatogram of native potato starch, had disappeared after α-amylolysis both in native and freeze-dried granules (chromatograms not shown). The initial weight average molar mass of potato starch was 15×10^7 g/mol. This molar mass decreased with increasing extent of hydrolysis to 8×10^7 (DE 10), 7×10^7 (DE 15) and 5×10^7 g/mol (DE 20). Originally potato starch was composed of 28% amylose (Tab. 2). The amylose content decreased with increasing DE due to depolymerisation. No difference was detected in the amount of hydrolysis of amylose between the native and freeze-dried starches, but the sugar contents were higher in all samples prepared from native starch (Tab. 2). In both centrifugation residues the sugar content increased with increasing DE, demonstrating that the washing was not sufficient enough especially when a higher amount of hydrolysis products was formed (DE 20). The results indicated also that more low molar mass reaction products were formed in the hydrolysis of native potato starch than in the case of freeze-dried starch. The water contents of the freeze-dried samples were higher than those of the native samples, although the difference was not big (Tab. 3).

The calorimetric traces of the solid residue films showed very clear transitions between 0 °C and 100 °C (Figs. 2 and 3). The transition became more pronounced with increasing DE, but in all cases it was much more clear than in the original starches (original starches not shown in Figs. 2 and 3). Assuming that the water contents of the various films were the same, the overall behaviour – decrease in T_g and more clear transitions with increasing DE – was induced by the decrease in the molar mass of starch and by the saccharides produced during hydrolysis. When comparing the films prepared from the native and freeze-dried residues, the sugar content increased with decreasing T_g in both cases (Tabs. 2, 3). Furthermore, the T_g's of the native starch films were significantly lower, which is in agreement with the higher sugar contents detected, and in fact also with the actual behaviour of the films (higher flexibility). Moreover, the films having

Tab. 3. Glass transition temperature (T_g) and water content of the film made of the solid residue from native (N) and freeze-dried (FD) potato starch hydrolysates with DE 10, 15 and 20.

Sample	T_g [°C]		Water content [%]	
	N	FD	N	FD
Potato starch	137	131	10	12
Solid residue (10)	28	70	10	11
Solid residue (15)	17	59	11	12
Solid residue (20)	7	27	11	14

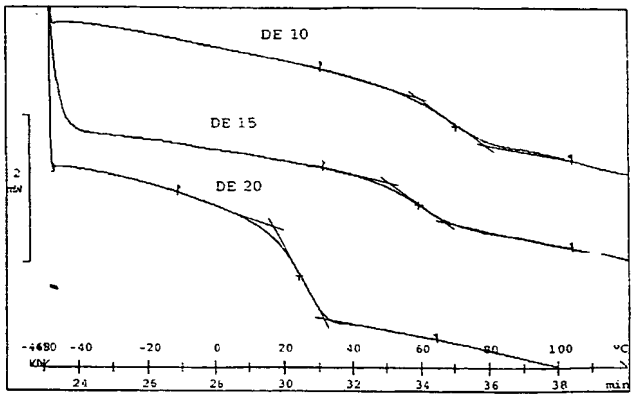

Fig. 2. DSC traces of the films prepared from the solid residue of freeze-dried starch. DE values are shown in the figure.

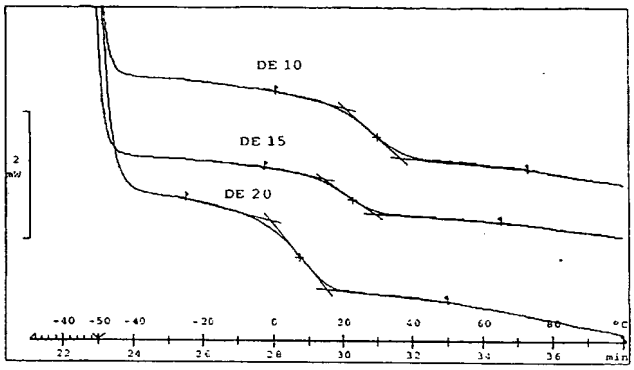

Fig. 3. DSC traces of the films prepared from the solid residue of native starch. DE values are shown in the figure.

about 5% of sugar showed T_g's at 17 °C and 27 °C, which are rather close to each other ($DE_{native\ solid\ residue}$ = 15 and $DE_{freeze\text{-}dried\ solid\ residue}$ = 20). Glass transition temperatures of commercial maltodextrins made of cereal and potato starches were recently reported [20]. The comparison with the results in the present study is difficult because of the unknown saccharide composition of the maltodextrins used in [20]. A similar decrease of the T_g with increasing DE was, however, observed in both cases.

4 Conclusions

Freeze-drying greatly improved α-amylase accessibility of native potato starch granules. Based on hydrolysis products and behaviour of the hydrolysates the hydrolysis mechanism of native starch differed from that of freeze-dried starch. After removing most of the sugars from the hydrolysis products all hydrolysates prepared from potato starch were able to form good quality films. For the film-casting process point of view the average molar mass de-

fined the highest solids content, which could be used in the casting procedure but the mechanical behaviour of the films was mostly dependent on the content of small sugars and other saccharides produced by hydrolysis.

Acknowledgements

The authors thank Dr. *Tapani Suortti* for the SEC analysis.

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(Received: April 4, 2001)

(Revision received: August 25, 2001)